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⑯ **Hair dye compositions.**

⑰ A bi-liquid oxidation type hair dye composition comprises ammonia as an alkali agent, and a specified water-soluble ammonium salt such as ammonium nitrate or ammonium chloride etc.

Since the composition enables hair-dying at a low pH level, hair or skin will never be damaged.

### BACKGROUND OF THE INVENTION

#### i) Field of The Invention:

This invention relates to a hair dye composition, and more particularly to a bi-liquid oxidation type hair dye composition which comprises a specified salt and ammonia, thereby achieves decoloration or hair dye in a deep color tone at a comparatively low pH level.

#### ii) Description of The Prior Art:

In a broad sense, so-called hair dye compositions include "a hair dye composition" for dying hair and "a bleach composition" for decoloring hair. In this specification, hair dye compositions include both categories. These hair dye compositions are used for the purpose of beauty treatment, and include so-called "white-hair dye compositions" to dye white hair to a desired color such as black, black-brown or blonde etc., so-called "fashion dye composition" to dye hair to a brighter color and so-called "white-hair/fashion dye compositions" to cover both functions.

These dye compositions are required to color whole hair or a part of hair to be dyed completely and securely, and to give a natural feeling.

The hair dye compositions used for such purposes include oxidation type permanent hair dye compositions and non-oxidation type semi-permanent hair dye compositions or temporary hair dye compositions (hair colors). Among which, bi-liquid oxidation type permanent hair dye compositions which comprise the color lotion containing dye-intermediates and an alkali agent, and the oxidizer containing an oxidant, are the most popular, since they offer more plentiful color tones than those of other type hair dyes, and also satisfy the above-mentioned requirements.

A bi-liquid oxidation type hair dye composition decomposes compounds such as peroxide of an oxidant with an alkali agent to generate oxygen, which makes decomposition/decoloration of melanine, and produces the oxidized dye by oxidation/polymerization of dye-intermediates, resulting in hair-dying. Therefore, if the oxidation/polymerization and the melanine decomposition are insufficient, the dyed hair shows no deep and natural tone with incongruity. These two reactions are strongly dependent on pH values. Since no satisfactory result is obtainable at acidic and neutral pH levels, the pH value is generally fixed at 10 or more.

However, hair treatment at a high pH level damages hair and skin considerably, while a lower pH value makes the dying effect inferior. Thus, both functions had not been satisfied at a time.

#### SUMMARY OF THE INVENTION

Under such circumstances, the inventors have studied to solve the above defects and found that use of ammonia as an alkali agent with a water soluble ammonium salt shows an excellent dying effect even at a low pH level, resulting in the production of a new hair dye composition without damages of hair or skin.

Accordingly, an object of this invention is to provide a bi-liquid oxidation type hair dye composition in which is contained ammonia as an alkali agent, and a water-soluble ammonium salt.

#### DETAILED DESCRIPTION OF THE INVENTION

##### AND PREFERRED EMBODIMENTS

Water soluble ammonium salts usable in this invention are, for example, ammonium chloride, ammonium citrate, ammonium oxalate, ammonium tartrate, ammonium bicarbonate, ammonium bisulfate, ammonium nitrate, ammonium carbonate, ammonium sulfate, ammonium phosphate, etc., and especially ammonium chloride and

ammonium nitrate are preferable since they have good dyeability. Other ammonium salts are rather inferior to those salts in view of dyeability and have some possibility to occur exothermic problem. Such a water-soluble ammonium salt may be incorporated in either or both of the color lotion and the oxidizer. It is desirable to adjust its pH level in the hair dye mixture to be 1 to 5 weight percent, when both of the color lotion and the oxidizer are mixed at the time of use, while no satisfactory effect appears at a pH of less than 1 weight percent, and no better result is also obtainable at a higher level than 5 weight percent.

The quantity of ammonia incorporated in the color lotion should be adjusted as to keep the pH of above hair dye composition mixture at 7 to 9.5.

In addition, the conventional oxidation type hair dye bases are mixed in the color lotion and in the oxidizer. The oxidation type hair dye bases include dye-intermediates, oxidants and also reactive compounds as couplers (modifiers) used together as occasion demands. Generally used dye-intermediates include para and other forms of such compounds as p-phenylenediamine, toluene-2, 5-diamine, N-phenyl-p-phenylenediamine, 4,4'-diaminodiphenylamine, p-aminophenol, p-

methylanilphenol, o-phenylenediamine, toluene-3, 4-diamine, o-aminophenol, p-chlor-o-phenylene diamine, p-amino-o-cresol, o-chlor-p-phenylenediamine, phloroglucinol, pyrogallol, 3,3'-iminodiphenyl, diphenylamine, 2,6-diaminophthidine, p-aminophenylsulfamic acid, etc. As couplers (modifiers), phenols and meta forms of such compounds as m-phenylenediamine, toluene-2, 4-diamine, p-methoxy-m-phenylenediamine, m-aminophenol, alpha-naphthol, resorcinol, hydroquinone, catechol, etc., are generally used. Among those couplers, in the case to dye black, chestnut, brown or blonde, p-phenylenediamine, toluene-2,5-diamine is especially important. Also, as oxidants, hydrogen peroxide, sodium perborate, urea peroxide, sodium percarbonate, sodium tripolyphosphate peroxide, sodium pyrophosphate peroxide, sodium orthophosphate peroxide, sodium silicate peroxide additive, sodium sulfate sodium chloride peroxide additive, etc., are used. In addition to the above compounds, the following materials as the dyes which influence the hair color tones without direct relation to the reaction of color formation can be added in order to keep the quality of hair dye and enhance its usefulness; for example, nitro-dyes such as nitro-p-phenylenediamine, p-nitro-o-phenylenediamine, 2-amino-4-

nitrophenol, 2-amino-5-nitrophenol, 4-amino-2-nitrophenol, etc., and direct dyes such as picramic acid, picric acid, 1,4-diaminoanthraquinone, etc.; surfactants such as nonion surfactants, anion surfactants, cation surfactants, amphoteric surfactants, etc.; surfactants such as nonion surfactants, anion surfactants, cation surfactants, amphoteric surfactants, etc.; solvents such as propylene glycol, glycerin, urea, etc.; lower alcohols such as ethyl alcohol, isopropyl alcohol, etc.; viscosity compensators such as hydroxy ethylcellulose, methyl cellulose, cationic high polymer compounds, higher alcohols, etc.; colors, sun-screen agents, antioxidants, preservatives, pearl agents, lotion agents, stabilizers, osmotic agents, moisturizers, haircare agents, perfume oil, vaselin, liquid paraffin and other materials. In the next, the actual cases are explanatory.

#### Example 1

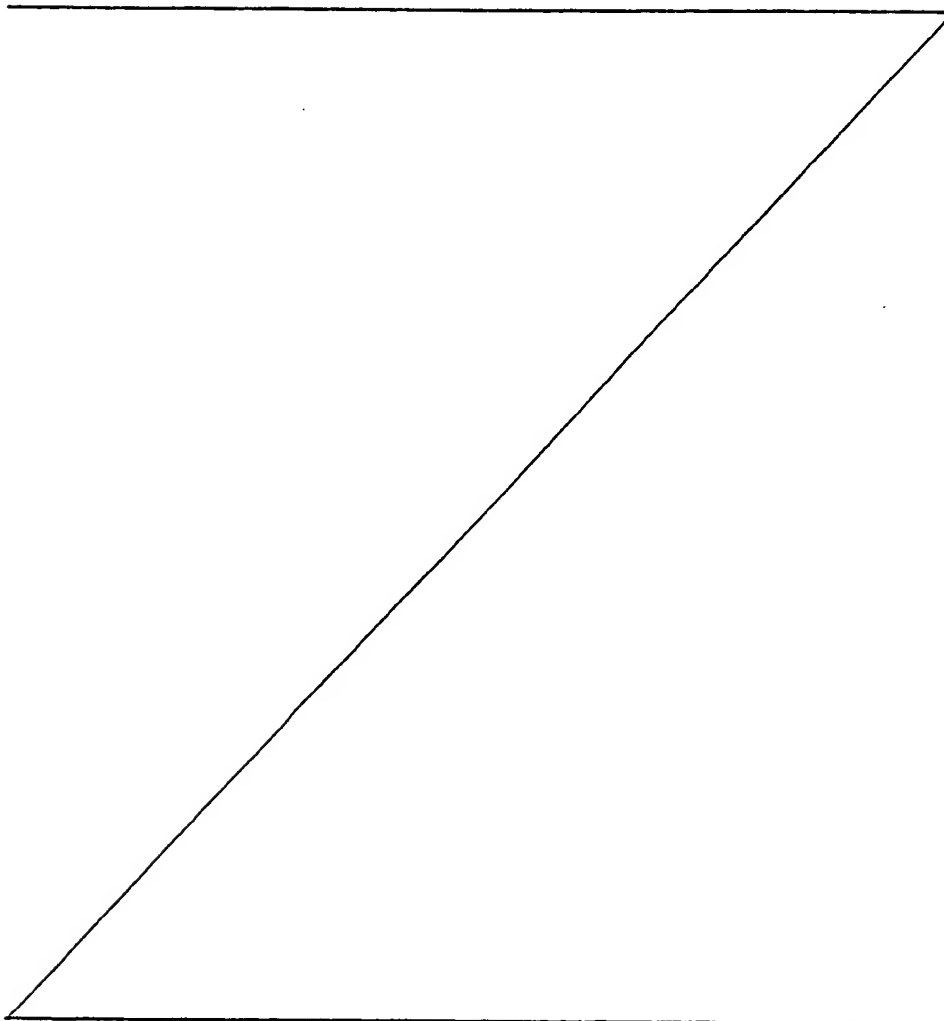
Bi-liquid type bleach compositions with the following formulations were prepared, and degrees of decoloration and degrees of smooth combing (degrees of hair damage) were determined.

##### (1) Bleach Compositions

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Color lotions; as shown in Table 1.

Oxidizers;      peroxide 6%  
                  phosphoric acid adjusted  
                  at pH 4;  
                  purified water; balance







## (2) Treatment Procedure

Black virgin hair of 20 cm long was washed with 0.5 % lauryl sodium sulfate aqueous solution, and air-dried to prepare the test hair. Twenty grams of the test hair was bundled, and spread with the same volume mixture of a color lotion and an oxidizer (pH 8.8) as a bleach at the bath ratio of 1:1, and allowed to stand for 30 min. The treated hair was rinsed with running water at 40°C, and washed with 0.5% of lauryl sodium sulfate aqueous solution followed by again rinsing with running water and air-drying.

## (3) Determination of Decoloration Degrees

The brightness of hair after the decoloration treatment was determined with Colorimeter Computer ND-1010C (Nippon Denshoku Kogyo K. K.). The L values in Table 2 indicate the brightness degrees, and higher values mean brighter degrees of decolored hair.

## (4) Combing Force

The bundle of decolored hair was combed with a comb fixed at the movable part of a tension tester (Tokyo Sokki UTM-II type), and the tension loaded on the hair bundle was determined as the combing force. The

combing force in Table 2 are average values and deviations for 20 times of combing.

(5) Results

Table 2

Assay	<u>Control</u>		<u>Products of This Invention</u>								
	A	B	C	D	E	F	G	H	I	J	K
Decoloration degree (L value)	24.8	43.8	44.5	45.8	45.5	44.0	39.0	38.0	38.7	37.5	38.5
Combing force (g)	240 +50	170 +20	168 +20	170 +30	185 +50	172 +30	180 +40	178 +30	170 +30	173 +30	175 +30

Example 2

Bi-liquid oxidation type hair dye compositions of the following formulations were prepared for dying hair, and the dying degrees of white human hair and the combing forces were determined.

(1) Hair Dye Compositions

Color lotions: as shown in Table 3.


Table 3

Ingredients (%)	Control	Products of Products of This Invention						
	L	M	N	O	P	Q	R	S
p-Phenylenediamine	2	2	2	2	2	2	2	2
o-Aminophenol	1	1	1	1	1	1	1	1
m-Phenylenediamine	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2
Ammonium nitrate	-	3	-	-	-	-	-	-
Ammonium chloride	-	-	3	-	-	-	-	-
Ammonium carbonate	-	-	-	3	-	-	-	-
Ammonium bisulfate	-	-	-	-	3	-	-	-
Ammonium bicarbonate	-	-	-	-	-	3	-	-
Ammonium sulfate	-	-	-	-	-	-	3	-
Ammonium Acetate	-	-	-	-	-	-	-	3
Oleic acid	10	10	10	10	10	10	10	10
Polyoxyethylene (10) oleylether	4.5	4.5	4.5	4.5	4.5	4.5	4.5	4.5
Polyoxyethylene (2) oleylether	4.5	4.5	4.5	4.5	4.5	4.5	4.5	4.5
Propylene glycol	15	15	15	15	15	15	15	15
Tioglycolic acid	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5
Sodium edetate	2	2	2	2	2	2	2	2
Perfume oil	0.3	0.3	0.3	0.3	0.3	0.3	0.3	0.3
Aqueous ammonia	Adjusted pH to 9	-do-	-do-	-do-	-do-	-do-	-do-	-do-
Purified water	Balance	-do-	-do-	-do-	-do-	-do-	-do-	-do-

Oxidizers:            peroxide 6%

                      phosphoric acid adjusted at

                      pH 9;

                      purified water; balance

(2) Hair Treatment Procedure

Same as (2) of Example 1 except the test hair,  
for which white human hair of 20 cm long was used.

(3) Determination of Dying Degrees

Same as (3) of Case 1, but lower L values in  
Table 4 indicate darker and deeper colors.

(4) Determination of Combing Forces

Same as (4) as Example 1.

(5) Results

Table 4

Assay	Control	Products of This Invention						
	L	M	N	O	P	Q	R	S
Dying degree (L value)	23.2	13.1	14.0	15.8	16.2	15.8	16.5	16.0
Combing force (g)	310 ±50	200 ±20	200 ±40	200 ±10	200 ±20	200 ±20	200 ±20	200 ±10

**Example 3**

Hair was dyed with the bi-liquid oxidation type hair dyes used in (1) of Example 2, and the color tones and touch feels of dyed hair were evaluated by 20 female panelers.

(1) Hair Treatment Procedure

Same as (2) of Example 2.

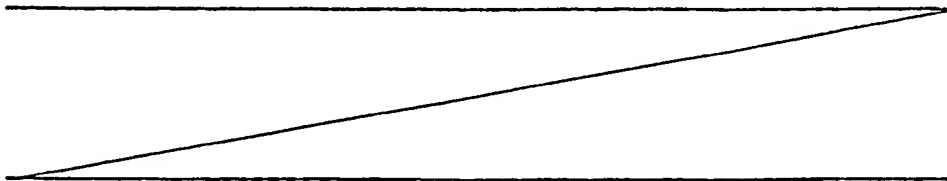
(2) Evaluation of Color Tones of Dyed Hair

Twenty women panelers evaluated the darkness degree comparing a test hair and the control both of which were dyed with hair dyes in Table 5.

(3) Evaluation of Touch Feels of Dyed Hair

Twenty female panelers evaluated the following items comparing a test hair with the control.

- 1) Softness
- 2) Smoothness
- 3) Combing condition



## (4) Results

Table 5

Items of Evaluation	<u>Products of This Invention</u>		
	M	N	O
Darkness	18	16	15
Softness	17	17	15
Smoothness	18	17	14
Good combing	18	16	13

The above figures indicate the number of evaluators who elect a product of this invention (M, N or O) as superior to the control L.

\* The evaluation was made at N=20.

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## WHAT IS CLAIMED IS:

1. A bi-liquid oxidation type hair dye composition consisting of a color lotion and oxidizer, which comprises ammonia as an alkali agent and a water-soluble ammonium salt.
2. A bi-liquid oxidation type hair dye composition according to Claim 1, wherein the water soluble ammonium salt is ammonium nitrate or ammonium chloride.
3. A bi-liquid oxidation type hair dye composition according to Claim 1 or 2, wherein pH of a mixture of the color lotion and oxidizer is 7 to 9.5 and the mixture contains 1 to 5 weight percent of a water-soluble ammonium salt.
4. A bi-liquid oxidation type hair dye composition according to Claim 1, 2 or 3, wherein the color lotion and oxidizer comprise p-phenylene-diamine or toluene-2,5-diamine as coupler respectively, and the water soluble ammonium salt is selected from ammonium chloride and ammonium nitrate.





DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.4)
X	DE-A-2 307 596 (WELLA AG) * Example 5 *	1,2,4	A 61 K 7/13
X	FR-A-1 365 276 (THE GILLETTE CO.) * Page 2, left-hand column, lines 19-58; page 3, left-hand column, lines 38-58 *	1-3	
Y		1-4	
X	DE-A-2 028 818 (THE GILLETTE CO.) * Example 1 *	1,3	
Y		1-4	TECHNICAL FIELDS SEARCHED (Int. Cl.4)
X	US-A-3 857 674 (FORSTHOFF et al.) * Examples 1-5 *	1,3	A 61 K
The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 12-02-1986	Examiner FISCHER J.P.
<p><b>CATEGORY OF CITED DOCUMENTS</b></p> <p>X : particularly relevant if taken alone  Y : particularly relevant if combined with another document of the same category  A : technological background  O : non-written disclosure  P : intermediate document</p> <p>T : theory or principle underlying the invention  E : earlier patent document, but published on, or after the filing date  D : document cited in the application  L : document cited for other reasons</p> <p>a : member of the same patent family, corresponding document</p>			

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54 Hair dye compositions.

57 A bi-liquid oxidation type hair dye composition comprises ammonia as an alkali agent, and a specified water-soluble ammonium salt such as ammonium nitrate or ammonium chloride etc.

Since the composition enables hair-dyeing at a low pH level, hair or skin will never be damaged.

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